# THE USE OF CALORIMETRY FOR FIRE MATERIALS RESEARCH

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## ABSTRACT

Research to improve the fire performance of materials requires tools to measure their flammability properties and validated fire growth models to predict fire behavior of the materials in specific fire scenarios using the measured properties as inputs to the models. One of the key flammability properties is heat release rate during free-burning or radiatively-assisted burning. Since the available amount of a new experimental material is generally quite limited, a small scale calorimeter, using a small amount of a sample, is used in fire research. The currently available, small scale calorimeters such as the Cone Calorimeter are capable of measuring not only time-dependent heat release rate but also many other flammability properties. Using such a device, this presentation will describe unique trends of heat release rate, specific heat of combustion, and others flammability properties of polymeric materials as they vary with the nature of the materials.

Polymers can be divided into two categories on the basis of degradation behavior. One does not generate any char during burning, e.g., polymethylmethacrylate; the other does generate char, e.g., wood or polycarbonate. For the former type sample, heat release rate under a constant external radiant flux increases rapidly with time after ignition but this increase gradually becomes less and eventually, asymptotically heat release rate reaches a constant value. On the other hand, there are two peaks in heat release rate for char forming polymers at a continuous constant external radiant flux. One appears shortly after ignition and then the heat release rate decreases rapidly with time due to the formation of a heat insulating char layer near the sample surface. If the back side of the sample is insulated, after the thermal wave reaches there, the sample heats up more and subsequently the degradation (if the remainder of the sample is not converted to char) is accelerated and heat release rate starts to increase again until the sample is significantly consumed. Similar behavior is often observed for the heat release rate of fiber-reinforced composite materials with a non char-forming polymer resin. In this case, the polymer resin layer near the irradiated surface degrades rapidly and heat release rate increases with time. After it is consumed, glass fiber layers act as an insulation layer and also acts as a physical barrier to the transport of degradation products from below the layer to the surface. Then, heat release rate decreases with time until delamination of the glass fiber layer to expose polymer layer below the glass layer or after the thermal layer reaches the unexposed back surface.

There are many different approaches to the flame retarding of polymers such as the enhancement of char formation, addition of halogenated compounds or halogenated elements to polymer chain, the formation of an intumescent layer and the addition of a heat sink such as aluminum trihydrate. These different flame retardants generate different trends of heat release rate curves and different characteristic heat releases. For example, the addition of brominated or chlorinated flame retardant additives to polymer samples decreases heat release rate significantly at a constant external radiant flux. However, mass loss rate does not change significantly with or without the halogenated flame retardant additives. The additives decrease significantly the specific heat of combustion (heat release rate divided by weight loss rate) and total heat release but they tend to increase CO and soot yields. These trends indicate that these additives tend to suppress gas phase oxidation reactions (by scavenging radical species). Our new char-forming/enhancing additives to non char-forming polymers significantly reduce heat release rate, mass loss rate, total heat release but do not have any significant effects on specific heat of combustion and CO and soot yields. The addition of the same additives to char-forming polymers significantly increases char yield and reduces heat release rate, total heat release, mass loss rate and also specific heat of combustion.

The addition of silicone to non char-forming polymers show different trends from the addition of halogenated flame retardants or the char-forming additives. It does not generate any char but significantly reduces heat release rate and mass loss rate. However, total heat release, specific heat of combustion, and CO and soot yields do not change significantly. These samples burn less vigorously than the samples without addition of silicone but they burn longer. The formation of a thin layer near the sample surface is observed and it appears that this layer interferes with the supply of combustible degradation products to the gas phase.

Other unique cases of heat release rate will be presented. One of them is simultaneous burning of two sides over a thermally thin material when both sides are exposed to a constant external radiant flux. Generally, only one side of a sample surface is exposed to external radiation. However, it is reported that heat release rate from a thermally thin material burning on both sides is more than twice the value seen when the conventional one side is burning. This is interpreted as a consequence of the Arrhenius temperature dependence of the gasification rate of the material. Another interesting case is the effect of sample size on heat release rate for a horizontally mounted polymer sample. The comparison of heat release rate curves of polycarbonate/silicone copolymer samples (generate intumescent char) between 10 cm square, 40 cm square, and 60 cm square at external radiant flux of 30 kW/m$^2$ shows that their peak heat release rates are about the same as each other but the total heat release per unit surface area tends to be about 50% higher for the two large samples than for the 10 cm square sample. Also, sample weight losses for the two large samples at the end of a test are about 30% higher than that for the small sample.